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Specification

1. Title of the Invention

HYDROPHILIC FILM LAMINATE

2. Claim

A hydrophilic film laminate comprising: a substrate; and a film provided on the substrate, the film having been hydrophilified by irradiating a hydrolyzate of a tetraalkoxide of titanium with ultraviolet light.

3. Detailed Description of the Invention

The present invention relates to a hydrophilic film laminate. More particularly, the present invention relates to a hydrophilic film laminate comprising: a substrate; and a film provided on the substrate, the film having been hydrophilified by irradiating a hydrolyzate of a tetraalkoxide of titanium with ultraviolet light.

A hydrolyzate of a tetraalkoxide of titanium is generally said to be water repellent although the water repellency varies depending upon the degree of hydrolysis. Specifically, the tetraalkoxide of titanium, when coated on various substrates, such as textiles, leathers and metals, is hydrolyzed upon exposure to moisture in the air to form a film of a complicate polycondensation product. It is well known that, by virtue of excellent water repellency, this film is utilized as a water repellent for the substrate.

By contrast, the present inventors have surprisingly found that exposure of the polycondensation product to ultraviolet light results in hydrophilification of exposed areas, which has led to the completion of the present invention.

Thus, according to the present invention, there is provided a hydrophilic film laminate comprising: a substrate; and a film provided on the substrate, the film having been hydrophilified by irradiating a

hydrolyzate of a tetraalkoxide of titanium with ultraviolet light.

Tetraalkoxides of titanium usable in the present invention are represented by general formula (1):

$$Ti(OR)_4 \qquad (1)$$

wherein R represents an alkyl group having 1 to 36 carbon atoms with $-CH_3$, $-C_2H_5$, n-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_6H_{13}, and iso-C_8H_{17} being preferred.

Ultraviolet irradiation is generally carried out in such a state that the hydrolyzate is provided on the substrate. A solution of several % by weight of the titanium tetraalkoxide dissolved in a single solvent or a mixed solvent selected from, for example, alcohols, such as methyl alcohol, ethyl alcohol, propyl alcohol, and butyl alcohol, and aromatic hydrocarbons, such as benzene, hexane, is coated on a substrate by spraying or by using a coater, such as a wire bar coater, a doctor blade, or a gravure coater, followed by hydrolysis at room temperature. If necessary, heating may be carried out by increasing desolvation rate.

It is also possible to use a reaction of vapor of a tetraalkoxide of titanium with water vapor, that is, the so-called "chemical gas phase deposition" and the like.

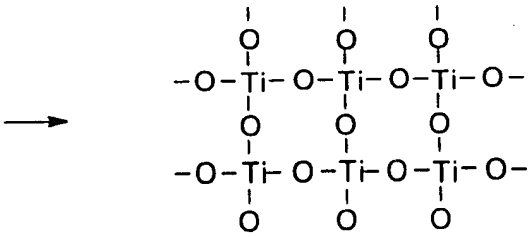
The hydrolyzate of tetraalkoxide of titanium thus formed is said to have various compositions according to the degree of hydrolysis. For example, the tetraalkoxide of titanium is hydrolyzed as represented by formulae (2) to (5).

$$Ti(OR)_4 + H_2O \rightarrow Ti(OR)_3OH + ROH \qquad (2)$$

$$Ti(OR)_3OH + Ti(OR)_4 \rightarrow (RO)_3TiOTi(OR)_3 + ROH \qquad (3)$$

$$x(RO)_3TiOTi(OR)_3 + xH_2O \rightarrow [\text{-}Ti(OR)_2O\text{-}]_2x + 2xROH \qquad (4)$$

$$[\text{-}Ti(OR)_2O\text{-}]x + xH_2O$$



(5)

The hydrolyzates represented by formulae (2) to (5) are formed in a

thickness of not more than 1000 Å on the substrate. Upon exposure of the thin hydrolyzate layer to ultraviolet light, the exposed areas are hydrolyzed. The reason for this has not been fully elucidated yet.

However, it is considered that, for example, titanium oxide present in the hydrolyzate functions as a sensitizer for photo-oxidation of an unreacted alkyl or aryl group to induce a chemical or physical change of the hydrolyzate.

As the substrate used in the present invention, moldings of synthetic polymers, metals, and various inorganic materials, and/or composites of these materials may be properly utilized according to applications of the product.

Ultraviolet irradiation may be carried out, for example, by simply irradiating the hydrolyzate with ultraviolet light from various mercury lamps. The ultraviolet irradiation time may vary depending upon the intensity of the ultraviolet light. In the case of an irradiation energy of 6 mW/cm^2 (a UV meter manufactured by Oufu Seisakusho; light wavelengths to which the object is sensitive = 300 to 400 mμ), the effect begins to be developed at an irradiation time of about 30 sec, and, when the irradiation time generally exceeds about 3 min, is saturated.

The present invention is based on such finding that exposure of hydrolyzates of tetraalkoxides of titanium, which have hitherto been said to have water repellency, to ultraviolet light causes the exposed areas to be hydrophilified. Examples of applications in which the laminate of the present invention is utilizable are as follows.

(1) Hydrophobic surfaces can be hydrophilified without sacrificing the texture of substrates.

(2) Hydrophobic surfaces of polyester films or the like can be simply hydrophilified to improve antifogging properties, adhesion, and printability.

(3) Hydrophobic areas and hydrophilic areas may be formed in response to image information. Therefore, the laminate of the present invention can be utilized for the fixation of image information by ink development and as lithographic plates.

(4) The laminate of the present invention can be utilized as a photoresist film provided on various metallic thin films and makes it possible to form metallic thin films having a desired shape.

The present invention will be further described with reference to the following examples.

Example 1

A monomer, a tetramer, and a decamer of tetra-n-titanate (hereinafter abbreviated to "TBT") were dissolved in a mixed solvent composed of hexane and isopropyl alcohol (weight mixing ratio = 1 : 3) to a concentration of 3% by weight.

The TBT solutions were coated on a 75 μm-thick polyester film by means of a #5 wire bar coater and a #10 wire bar coater, and the coatings were hydrolyzed under conditions shown in Table 1 to form thin films of hydrolyzates of TBT.

Next, the thin films were irradiated with ultraviolet light from a 400 W low pressure mercury lamp (light energy on the exposed areas = 6 mW/cm^2) under conditions shown in Table 1. After the irradiation, the contact angle of the unexposed area with deionized water and the contact angle of the exposed area with deionized water were measured. The results are shown in Table 1.

Table 1: Contact angle (°) of hydrolyzates of TBT

TBT film thickness, Å	Conditions for hydrolysis of TBT	UV irradiation time, min	Contact angle of hydrolyzates of TBT, °					
			Monomer		Tetramer		Decamer	
			Unexposed area	Exposed area	Unexposed area	Exposed area	Unexposed area	Exposed area
#5 bar coater (about 300 Å)	Air drying	1	47°	18°	72°	30°	63°	26°
		3		11°		15°		10°
		5		5°		13°		8°
	Air drying followed by drying at 110°C for 3 min	1	50°	36°	65°	30°	61°	23°
		3		10°		8°		15°
		5		8°		7°		10°
#10 bar coater (about 300 Å)	Air drying	1	46°	21°	76°	46°	53°	22°
		3		15°		39°		11°
		5		4°		12°		9°
	Air drying followed by drying at 110°C for 3 min	1	56°	21°	60°	25°	58°	26°
		3		11°		9°		14°
		5		9°		3°		7°

As is apparent from Table 1, the contact angle of the area unexposed to the ultraviolet light with water was at least 45° . On the other hand, the contact angle of the exposed area with water decreased with the irradiation time and, for an irradiation time of 5 min, became not more than about 10° , indicating that hydrophilic films having a significant effect were formed.

Example 2

A monomer of tetraisopropyl titanate (hereinafter abbreviated to "TPT") was dissolved in a mixed solvent composed of hexane and isopropyl alcohol (weight mixing ratio = 1 : 3) to a concentration of 3% by weight.

The TPT solution was coated on a 75 μm-thick polyester film by means of a #3 wire bar coater and a #5 wire bar coater, and thin films of hydrolyzate of TPT were formed under conditions shown in Table 2.

Next, the thin films were irradiated with ultraviolet light from a 400 W low pressure mercury lamp (light energy on the exposed areas = 6 mW/cm^2) under conditions shown in Table 2. After the irradiation, the contact angle of the unexposed area with deionized water and the contact angle of the exposed area with deionized water were measured. The results are shown in Table 2.

Table 2: Contact angle (°) of hydrolyzates of TPT

TPT film thickness, Å	Conditions for hydrolysis of TPT	UV irradiation time, min	Contact angle of hydrolyzates of TPT, °	
			Unexposed area	Exposed area
#3 bar coater (about 150 Å)	Air drying	1	47°	35°
		3		12°
		5		10°
#5 bar coater (about 300 Å)	Air drying	1	37°	30°
		3		15°
		5		7°

As is apparent from Table 2, the contact angle of the area unexposed to the ultraviolet light with water was at least 37° . On the other hand, the contact angle of the exposed area with water decreased with the irradiation time and, for an irradiation time of 5 min, became not more than about 10° , indicating that hydrophilic films having a significant effect were formed.